

High quality bio-oil from catalytic flash pyrolysis of lignocellulosic biomass over alumina-supported sodium carbonate

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ABSTRACT

Performance of a novel alumina-supported sodium carbonate catalyst was studied to produce a valuable bio-oil from catalytic flash pyrolysis of lignocellulosic biomass. Post treatment of biomass pyrolysis vapor was investigated in a catalyst fixed bed reactor at the downstream of the pyrolysis reactor. In-situ catalytic upgrading of biomass pyrolysis vapor was conducted in an entrained flow pyrolysis reactor by feeding a premixed feedstock of the catalyst and biomass. $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ was very effective for de-oxygenation of the pyrolysis liquid and oxygen content of the bio-oil was decreased from 47.5 wt.% to 16.4 wt.%. An organic rich bio-oil was obtained with 5.8 wt.% water content and a higher heating value of 36.1 MJ/kg. Carboxylic acids were completely removed and the bio-oil had almost a neutral pH. This bio-oil of high calorific low, low water and oxygen content may be an attractive fuel precursor. In-situ catalytic upgrading of biomass pyrolysis vapor produced a very similar quality bio-oil compared to post treatment of pyrolysis vapors, and shows the possible application of $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ in a commercial type reactor system such as a fluidized bed reactor.

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1. Introduction

Pyrolysis-oil (hereinafter “bio-oil”) produced with current flash pyrolysis technologies is not suitable for direct use as a transportation fuel or as a fuel additive. The presence of oxygenated compounds in the bio-oil mainly contributes to its deleterious properties, high viscosity, non-volatility, high acidity and resulting corrosiveness and extreme instability upon storage, lower energy density than the conventional fuel by 50%, incompatibility and immiscibility with fossil fuels, thermal instability and tendency to polymerize under exposure to air [1–5]. Catalytic de-oxygenation is considered as a first line option to overcome the problem characteristics of the bio-oil beside catalytic reformation of the large lignin derived molecules into useful products.

The challenge in de-oxygenation catalyst development is to design a catalyst that selectively removes the problematic oxygenates in the bio-oil. The oxygen may be given off by de-hydration, de-carbonylation and de-carboxylation leading to the formation of water, CO and CO_2 , respectively. The de-carboxylation is the preferred route for de-oxygenation in comparison to de-hydration as de-carboxylation allows retention of hydrogen in bio-oil, maximizes oxygen removal with minimal carbon loss and thereby increases heating value, decreases the aromatic compounds, minimizes the water content of the bio-oil, and decreases

its hydrophilicity. Hence, in order to retain maximum energy content in the bio-oil, selective scission of bonds should follow the order of $\text{C}-\text{C} > \text{C}-\text{O} > \text{C}-\text{H}$.

So far, catalyst studies for biomass pyrolysis have been mainly focused on zeolites (Y, ZSM-5, mordenite and beta), and mesoporous aluminosilicates. However, zeolites and aluminosilicates have not shown any promising results. Major drawbacks to use relatively small pore zeolites are; a significant decrease in organic yield due to the increase of the production of water and gases, and a rapid catalyst deactivation by coke deposition [6]. Alkali metals are found to be effective catalysts for H_2O and CO_2 gasification of carbon [7]. Lee et al. used Na_2CO_3 for the catalytic gasification of rice straw over nickel catalyst and formation of gas was significantly enhanced [8]. The effect of alkali compounds on the properties of bio-oil has not been studied systematically and there is very limited literature available on the effect of alkali compounds on bio-oil. Several researchers [9–12] used alkali compounds as a catalyst for biomass pyrolysis and found that alkali compounds lowered the temperatures of biomass devolatilization and decreased biomass conversion time, these effects were enhanced by increasing the basicity of alkali compound and the use of Na with respect to the K ion. Bradbury et al. found that the inorganic content in the biomass has a significant effect on the yield of gas and char, and concluded that increasing the inorganic contents in the biomass promotes the secondary cracking reactions that leads to the breakdown of higher molecular compounds to smaller ones [13]. It is well known that cations of alkali metal in biomass can affect thermal decomposition mechanism of fast pyrolysis and can form the natural polymer chains

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via primary fragmentation of the monomers [14]. Raveendran et al. claimed that the alkaline cations have a significant effect on the catalytic pyrolysis of biomass compared to anion of alkali metals [15].

Alkali metals can be applied directly for catalytic biomass pyrolysis but direct addition of alkali metal catalysts has several disadvantages, e.g. difficult and expensive recovery of the catalyst. To solve these problems, they can be supported on a catalyst carrier e.g. alumina and taking advantage of catalytic effects of both alumina and alkali metal. Very few studies could be found on active alumina which is a solid acid catalyst [16,17]. Larger pore size alumina has potential for reducing the coke formation and enhancing the organic liquid yield due to their lower acidity. Larger molecules, particularly lignin-derived compounds, can enter, reformulate and exit the bigger pores of alumina with lesser chances of coke formation and resulting blockage of the pores. To take advantage of larger pore size alumina and alkali metal, a novel alumina-supported sodium carbonate ($\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$) catalyst is developed based on systematic studies at laboratory scale with batch experiments using a 2 g biomass sample and a catalyst fixed bed reactor [18]. In the current work, $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ has been implemented in a bench scale unit of 1 kg/h biomass capacity that consists of an entrained flow pyrolysis reactor. Post pyrolysis vapor treatment which was carried out in a catalytic fixed bed reactor to study the effect of the catalyst temperature independent of the pyrolysis reaction and to isolate the catalyst/vapor contact problems may occur in case of in-situ application of the catalyst in entrained flow pyrolysis reactor. In-situ upgrading of pyrolysis vapors was carried out in the entrained flow pyrolysis reactor with premixed feedstock of catalyst and biomass to simulate the condition of a commercial system such as fluidized bed reactor. The entrained flow downer reactor configuration is selected because of easy operation handling and it demonstrated high heating rates of the biomass while maintaining good control of the reaction conditions for instance the residence time of reactants and products [19,20].

2. Materials and methods

For the production of bio-oil via catalytic flash pyrolysis of woody biomass, a continuous bench scale unit of 1 kg/h feedstock (biomass/and catalyst) capacity has been designed. A schematic of the unit is presented in Fig. 1. The feedstock (biomass or biomass/catalyst) is loaded into the feed hopper and fed to the entrained down flow reactor by a screw feeder and inert carrier gas (nitrogen). The pyrolysis reactor is consisted of a cylindrical quartz tube of 4.2 m length with an

internal diameter of 5 cm. The reactor is heated electrically through heating coils around the wall and the reactor temperature is controlled by thermocouples installed at various heights of the reactor. Feedstock enters the reactor at its top, and in a few seconds the thermochemical conversion of biomass particles takes place under inert atmosphere yielding a gas composed of condensables (bio-oil), non-condensables, and char.

The catalyst fixed bed reactor was used only for the post treatment of pyrolysis vapor and it was bypassed for in-situ upgrading of pyrolysis vapor in an entrained flow reactor. The fixed bed reactor is made of stainless steel, 300 cm length and 6 cm internal diameter. The reactor is heated electrically and the catalyst is loaded before the start of the experiment. The vapor residence time in the catalyst fixed bed reactor is less than half a second.

The vapors, gases and solids leaving the reactor enter tangentially into a cyclone that allows removal of solid particles up to 20 μm . The solids consist of char (ash and unconverted biomass) for non-catalytic experiments and char plus spent catalyst for in-situ catalytic experiments. Due to a wide particle size distribution of the biomass and the catalyst, it is difficult to design a very efficient cyclone, therefore fine particles are separated in a hot filter element at the downstream of the cyclone. A solid free gas is carried to two double tube heat exchangers (operated with a coolant mixture of glycol and water at -5°C circulating through outer tubes). In this section the condensable fraction of the gases is recovered as a liquid. Heavy and middle fractions of the condensable vapors are recovered in the first condenser and lighter fraction of the bio-oil is recovered in the second condenser. The gases leaving the condensers still carry a mist or fumes of product vapors that are recovered in a rotating particle separator (RPS) where they are impinged onto the surface of filter and can flow downwards out of the filter by gravity as a liquid. The oil separated by the filter element is collected at the bottom of the RPS and taken off at the end of the test run. The RPS is very efficient to capture the mist of oil vapors and nearly vapor free gas leaves the RPS and is taken off for gas analysis. Other operating conditions and parameters are listed in Table 1.

2.1. Biomass

The biomass used for the experiments consisted of wood fibers commercially available with trade name Lignocel by J. Rettenmaier & Söhne GmbH. The biomass particle size varied from 0.1 to 1 mm. The ultimate and proximate analyses are presented in Table 2.

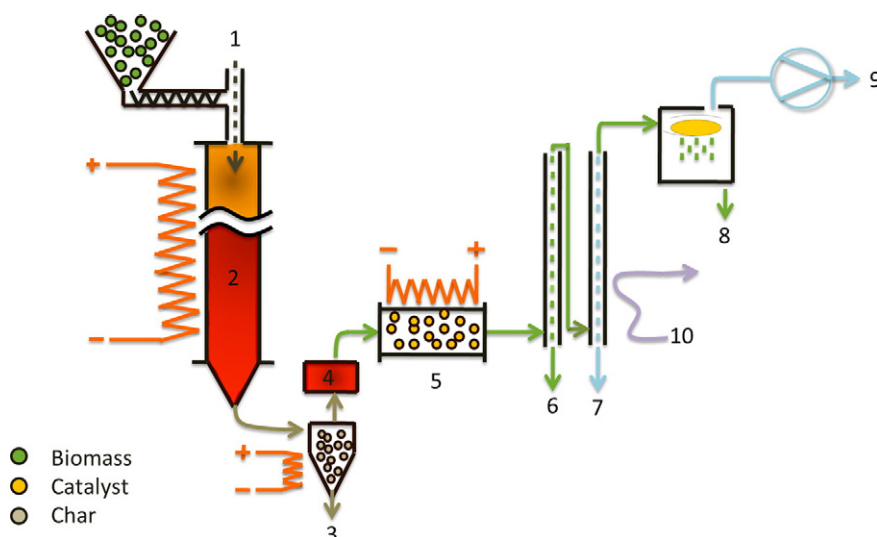


Fig. 1. Schematic presentation of the experimental setup. 1. Carrier gas (N_2). 2. Pyrolysis reactor. 3. Solid recovery. 4. Hot particle filter element. 5. Catalyst fixed bed reactor. 6–7–8. Liquid collection. 9. Gas to analysis unit. 10. Coolant.

Table 1
Operating conditions.

Reactor temperature	400–550 °C
Reactor pressure	1 atm
Feed hopper capacity	4 kg
Feedstock feed rate	1 kg/h
Biomass particle size range	150–1000 µm
Vapor residence time in reactor	2–4 s

2.2. Catalyst

$\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ was prepared by wet impregnation method. A $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ ratio of 1:2 by weight was used. Na_2CO_3 (ACS reagent grade > 99.5%) and $\gamma\text{-Al}_2\text{O}_3$ was obtained from Sigma Aldrich and Albemarle respectively. A saturated solution of sodium carbonate was prepared at room temperature (21 g Na_2CO_3 per liter of water) and heated to 60 °C. Alumina carrier ($\gamma\text{-Al}_2\text{O}_3$) was added to the Na_2CO_3 solution and stirred for 2 h keeping at 60 °C. After 2 h, the catalyst was dried in an oven at 105 °C to evaporate the water. Finally, the catalyst was calcined in an oven at 600 °C for 12 h and stored in a desiccator. Catalyst characterization has been described in detail by Nguyen et al. [18].

2.3. Product analysis

The non-condensable gases leaving the RPS primarily composed of carbon dioxide, carbon monoxide and C_1 , C_2 , and C_3 hydrocarbons. The volumetric flow rate of these gases is measured with a gas flow meter and a sample of this stream is pumped to an on-line gas analysis unit. Infrared analyzers are used to measure CO and CO_2 and a FID analyzer is used to measure hydrocarbons. The liquid is analyzed with an elemental analyzer to find out elemental composition. Water contents of the oil are quantified by Karl Fisher titration. A bomb calorimeter is used to determine the heating value of the bio-oil. An Agilent GC–MS is used to analyze the bio-oil and the NIST8 library is used to detect the components.

3. Results and discussion

For thermal (non-catalytic) pyrolysis experiments, the targeted maximum liquid yield was obtained at 500 °C reactor temperature and 4 s residence time of biomass/vapors in the reactor. Therefore, same operating conditions were used for the catalytic experiments in order to compare the effect of catalyst on nature and yield of different products of biomass pyrolysis. Catalytic experiments were conducted both for post treatment of biomass pyrolysis vapor in a catalyst fixed bed and for in-situ upgrading of pyrolysis vapor in an entrained flow reactor.

3.1. Post treatment of biomass pyrolysis vapors in a catalytic fixed bed reactor

A series of preliminary experiments was conducted to optimize the pyrolysis reaction conditions in the entrained flow reactor and the targeted maximum liquid yield was obtained at 500 °C reactor temperature and 4 s residence time of biomass/vapors. The produced vapor/gas

stream was passed over a fixed bed of 200 g of $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$. A catalyst/biomass ratio of 1:1 was used for present experiments. To achieve the desired catalyst/biomass ratio, an experimental run was set to feed 200 g of biomass to achieve 1:1 ratio of catalyst and biomass. Furthermore, a slight reduction in catalyst activity was observed due to coke formation at the catalyst when more than 200 g of biomass was fed in a single batch of experiment. The catalyst requires a continuous combustion of coke to maintain its activity that was not possible in current experimental scheme.

To study the effect of catalyst on biomass pyrolysis, several experiments were conducted with the fixed bed catalyst at 500 °C. The product yields on basis of dry initial weight of biomass are presented in Table 3. In contrast to thermal pyrolysis, catalytic pyrolysis resulted the phase separation of the liquid product; the liquid was instantaneously separated in aqueous and organic fractions upon condensation in the condenser. This phase separation made it possible to separate the organic fraction from the aqueous fraction. The whole liquid was transported to a conical separation flask, and the organic fraction was settled at the bottom of the flask and collected separately from the aqueous fraction. For thermal experiment, the water content of the liquid has been represented as the aqueous fraction but in practice there was no phase separation achieved in the absence of the catalyst. The implementation of the catalyst significantly altered the pyrolysis products. Total liquid was decreased from 58% to 32.4% and three times higher amount of gas was formed in the presence of the catalyst. The yield of organic liquid fraction was considerably reduced to 9.4% compared to that of 47.2% in non-catalytic experiment. The catalyst also led to the conversion of a part of pyrolysis vapors into the coke. Nguyen et al. have described that this coke has high oxygen content up to 41.5 wt.% and high amount of coke formed on catalyst contributes as a major de-oxygenation route [18]. The catalyst did not have any influence on the char yields, the char was recovered before the catalyst bed and the catalyst could not influence the primary conversion of the biomass. The effect of the catalyst on the gas composition is presented as the relative selectivity to CO, CO_2 and hydrocarbons. The type of the gaseous products formed (CO , CO_2 , C_xH_y) indicates the energy content of the bio-oil after de-oxygenation and cracking. The formation of CO and CO_2 will lower the oxygen content of bio-oil and the formation of C_xH_y will lower the energy content of the bio-oil due to the loss of hydrogen. The catalyst favored the formation of CO_2 and suppressed the CO formation although the formation of hydrocarbon was unavoidable because of the secondary cracking of the vapors. The gas formation and the coke formation are the two major routes for the de-oxygenation and the reduction in the liquid yield is obvious, however further development of the catalyst can increase the liquid yield by minimizing de-hydration and cracking reaction and by maximizing the decarboxylation reaction.

Table 4 shows the product energy distribution of post vapor treatment experiment based on the energy in the biomass fed. Overall 78% of the energy was recovered in the products and 22% of the energy was unrecovered either lost in aqueous liquid fraction, in conversion process or/and in missing mass. 20.9% of the energy was recovered in the bio-oil. The energy recovery from the byproducts (char, coke and gas) can make the process economically attractive in an integrated pyrolysis system to provide the heat required for thermal conversion of biomass.

Table 2
Ultimate and proximate analysis of biomass on weight basis.

Ultimate analysis			Proximate analysis			
C	H	O ^a	Moisture	Volatiles	Fixed Carbon	Ash
49.2	5.7	45.0	6.5	76.4	13.5	0.5

^a By difference.

Table 3
Product yield weight (%) for both thermal and catalytic pyrolysis.

	O.F. ^a	A.F. ^b	Coke	Char	Gas	C_xH_y	CO_2	CO
Thermal	47.2	21.7	0	16.2	11.6	1.9	4.7	5.1
Catalytic (500 °C)	9.4	23	7.1	18.4	30.2	4	14.4	11.8

^a Organic fraction of liquid.

^b Aqueous fraction of liquid.

Table 4
% energy recovery of catalytic pyrolysis products.

O.F.	Coke	Char	Gas	Overall energy recovery
20.9	10.5	27.3	19.3	78

The catalyst bed temperature can be operated independent of the pyrolysis reactor temperature and experiments were performed at different catalyst bed temperatures to study the effect of the reaction temperature on the liquid product. The catalytic experiments were performed at a catalyst bed temperature of 430, 475, 500 and 550 °C and biomass pyrolysis product distribution and gas composition are presented in Fig. 2a and b. The catalyst bed temperature had a very little effect on the product distribution and the gas composition. The organic liquid yield slightly increased with increasing the catalyst bed temperature and the highest organic yield was achieved at 500 °C. Further increase in the catalyst bed temperature was not beneficial and had negative impact on the organic liquid yield. Optimum organic yield achieved at 500 °C catalyst bed temperature was 9.4% and corresponding aqueous fraction yielded 23%. With an increasing catalyst bed temperature, there was a slight increase in the coke yield and the highest coke yield obtained at 550 °C was 8.2%. With increasing temperature

from 430 °C to 500 °C, the hydrocarbons and CO concentration in the gas increased and decreased when the temperature was further increased to 550 °C. The effect of increasing catalyst bed temperature on CO₂ was vice versa, the CO₂ yield decreased by increasing catalyst bed temperature from 430 °C to 500 °C and then slightly increased when catalyst bed temperature was further increased to 550 °C.

As the organic liquid fraction called bio-oil is of main interest, a detailed analysis of the bio-oil is presented in Fig. 2c. The aqueous fraction will be discussed later. The elemental composition and higher heating value of bio-oil are on dry basis. The catalyst application had a significant effect on the bio-oil properties and noticeable improvements in the bio-oil quality were achieved. No clear trends can be seen in the bio-oil properties with increasing catalyst bed temperature. As the maximum bio-oil yield was achieved at 500 °C with minimum oxygen content, it will be used for the comparison between the thermal and the catalytic pyrolysis experiments. Carbon content of the bio-oil increased from 46% to 75.5%, the hydrogen content increased from 6% to 7.6%. The water content of bio-oil decreased from 31.5 to 5.8% and the higher heating value increased from 17.8 MJ/kg to 36.1 MJ/kg. The most significant improvement was the high level of de-oxygenation achieved; 65% de-oxygenation was obtained as the oxygen content of the bio-oil decreased from 47.5% to 16.4%.

The experimental results show that Na₂CO₃/γ-Al₂O₃ had desired effect on the properties of bio-oil and a high quality bio-oil was achieved that can be further improved for fuel application. Na₂CO₃/γ-Al₂O₃ resulted in a very high de-oxygenation via gas and coke formation, although the bio-oil yield was lowered because of higher gas and coke formation but this lower bio-oil yield can be compensated by its superior quality, low oxygen contents and high energy density very close to that of fossil fuel. Na₂CO₃/γ-Al₂O₃ is an effective catalyst for de-oxygenation, it follows the ideal order of priority CO₂ > CO > CxHy aimed at removing maximum oxygen with single carbon atom and maximizing the hydrogen content in the bio-oil. Higher gas yield in the presence of Na₂CO₃/γ-Al₂O₃ is due to de-oxygenation and secondary cracking reactions of product vapors. Very low organic liquid yields obtained in the presence of the catalyst cannot be avoided if high de-oxygenation of the bio-oil is required because of the loss of carbon and hydrogen associated with various routes of catalytic de-oxygenation. The catalyst properties and process parameters may be further optimized to increase the bio-oil yield. An integrated heat recovery from combustible gases, char and coke can increase the overall process efficiency and economics.

3.1.1. Bio-oil characterization

The bio-oil obtained from the catalytic and non-catalytic pyrolysis of biomass was analyzed by GC–MS. As explained earlier whole liquid fraction was used for non-catalytic experiment and organic fraction (bio-oil) was used for catalytic experiment. A wide range of organic compounds are found in the bio-oil. The identified compounds of the organic phase are typically grouped as hydrocarbons, phenols, furans, carboxylic acids, alcohols, aldehydes, ketones, aromatics and PAHs (polycyclic aromatic hydrocarbons). In Fig. 3, the chemical composition of bio-oil has been described as total ion chromatogram area percentages of all the compounds and the compounds have been classified according to their chemical nature.

There is no clear trend found in the chemical composition of bio-oil with varying catalyst bed temperatures but there was clear difference in catalytic and non-catalytic bio-oils. Carboxylic acids were the most dominating compounds in non-catalytic bio-oil and acetic acid was the single most dominant compound found among all the acids. Na₂CO₃/γ-Al₂O₃ completely removed the acids from the bio-oil. This is the most significant improvement in the quality of bio-oil as acids are the main contributors for the acidity of the bio-oil [21] and removal of acids will lower the corrosivity and pH, and will improve the calorific value and handling properties of the bio-oil. Sugars being another contributor to the acidity of the bio-oil are completely removed in the

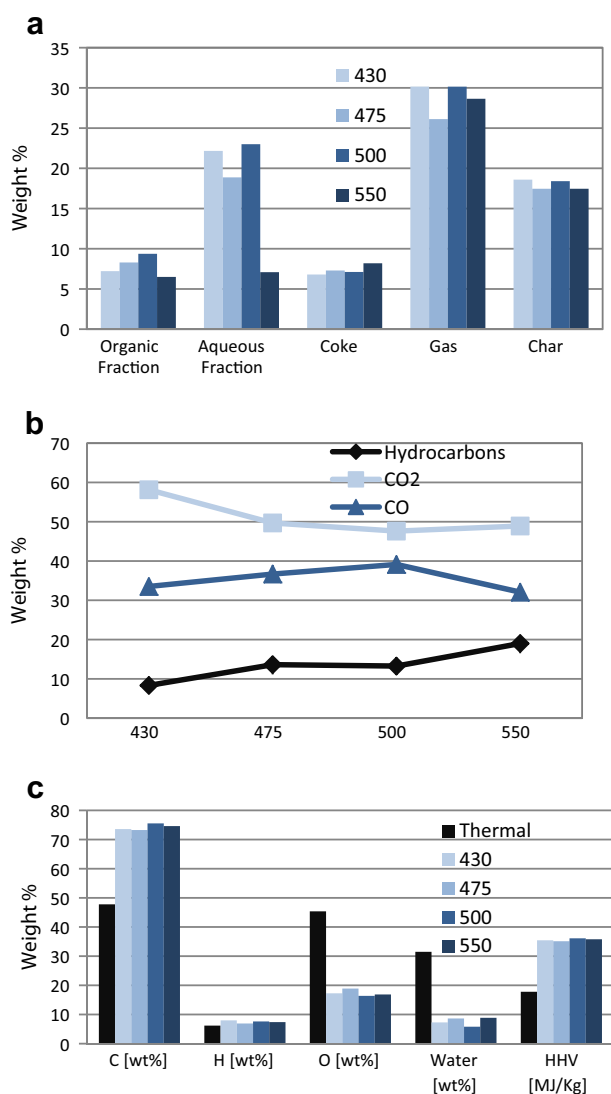


Fig. 2. a. Effect of the catalyst bed temperature (°C) on the product yields. b. Effect of the catalyst bed temperature (°C) on the gas composition. c. Effect of catalyst bed temperature (°C) on the characteristics of organic fraction of the liquid.

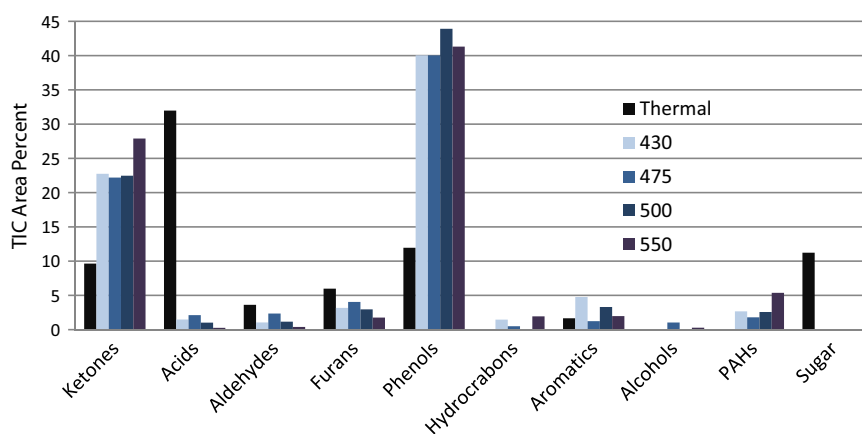


Fig. 3. GC–MS analysis of the organic liquid fraction of thermal and catalytic pyrolysis (for catalytic post treatment of pyrolysis vapors).

catalytic bio-oil. Removal of these two major contributors (acids and sugars) to the acidity of bio-oil is clearly reflected in acid measurements of the bio-oil presented in Table 5, and catalytic bio-oil is almost neutral in pH.

$\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ caused a significant reduction in the aldehydes. Reduction in the aldehydes is very good for the stability and shelf life of the bio-oil. Complete removal of the acids and reduction in the aldehydes can be attributed to the intermediate acidity of the alumina, which seems to be optimum to inhibit some of undesirable reactions that lead to formation of acids and aldehydes.

$\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ yielded high amounts of the phenols, a high value compound especially for resin and adhesive industry making the process economically attractive. Phenols are lignin derived product made by the cracking of the phenyl-propane units of the macromolecule lattice [21]. Huber et al. suggested that the aromatics, phenols and their alkyl substituted fractions are formed by recombination and cyclization reactions, via condensation from C2, C3 and C4 fragments which are the initial degradation product [22]. Apparently, $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ favored the formation of substituted phenols, such as alkylated and alkoxyphenols.

PAHs and aromatic compounds in the bio-oil are considered lignin derived products mainly by the decomposition of polysaccharides. No PAHs are found in non-catalytic bio-oil. $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ formed PAHs, mainly naphthalenes and substituted naphthalenes while all fractions of aromatic compounds increased in the presence of $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$. It seems that $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ stimulated the catalytic reactions that favor the formation of PAHs such as cyclization, aromatization, and condensation. Furthermore, alumina pores are large enough so that naphthalene and substituted naphthalenes can leave the pores after their formation before the polymerization of these products happened and caused coke formation. The large regular pores of alumina allow the diffusion of reactants in the catalyst and diffusion of the products out of catalyst, minimizing consecutive decomposition reactions [23]. The large pores of $\gamma\text{-Al}_2\text{O}_3$ allow more molecules to enter the catalyst and experience the cracking and reforming reactions and their subsequent aromatization. It seems that the $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ is able to catalyze reactions that can convert oxygenated compounds into aromatic hydrocarbons such as de-carboxylation, de-carbonylation, de-hydration and aromatization.

A noticeable effect was the increased formation of ketones in the presence of $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$. Ketones undergo condensation reactions and cause the formation of higher molecular weight components by polymerization reactions and increase viscosity [24]. Formation of ketones in the presence of $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ poses a challenge for the stability of the bio-oil. Ketones can be upgraded via post hydrogenation step to obtain liquid alkanes as described by Huber et al., this process involves aldol condensation and hydrogenation of ketones [22]. Nevertheless, increased ketones yield can be tolerated comparing the other benefits obtained in the presence of $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ for e.g. complete removal of acids, high heating value and high level of de-oxygenation.

The catalytic bio-oil obtained has a low water and oxygen content and is rich in organics which are attractive fractions for gasoline production via fluidized catalytic cracking (FCC)/hydrotreatment. The decrease in the content of oxygen, increase in hydrogen content and the concentration of molecules with more than six carbon atoms in the bio-oil could help reduce the amount of hydrogen needed for the hydrotreatment of this bio-oil and make it an attractive precursor for fuel application.

3.1.2. Characterization of the aqueous fraction

The aqueous fraction of the liquid obtained in the catalytic pyrolysis of biomass was analyzed for its water content and the chemical composition. The aqueous fraction consisted of 90–94% water (see Table 6) and the rest were organics. Due to the high water content of the aqueous fraction, the elemental composition cannot be obtained accurately. The organics present in the aqueous fraction are analyzed by GC–MS and compared with that of the bio-oil (organic fraction of the liquid) in Table 7. For this comparison, experiment conducted at a catalyst bed temperature of 500 °C was selected. Compounds in the aqueous fraction are the same as the organic components in the bio-oil except for the ketones and phenols. The ketones yield is much higher in the aqueous fraction and lower in the organic fraction while the phenols are significantly lower in the aqueous fraction and higher in the organic fraction. High polarity ketones are originated from the cellulose and hemicellulose components of biomass [25] and phenolic compounds are originated from lignin. Yields of other chemical compounds are altered only slightly. It is interesting to note that the catalyst has

Table 5
Acidity of bio-oil.

	Thermal	Catalytic at 500 °C
TAN ^a	159	3.45
pH	2.2–2.4	6.3

^a Total acid number of bio-oil based on standard ASTM 664.

Table 6

Water content of aqueous fraction of liquid obtained at different catalyst bed temperatures.

Catalyst temperature [°C]	Water content [wt.%]
550	90.7
500	93.7
475	91.4
430	92.9

Table 7

Comparison of organic compounds in the pyrolysis liquid.

	Ketones	Acids	Aldehydes	Furans	Phenols	Hydrocarbons	Aromatics	Alcohols	PAHs
Organic fraction	22.5	1.0	1.2	3.0	43.9	0.0	3.3	0.0	2.6
Aqueous fraction	55.8	1.7	0.5	3.3	11.3	1.2	0.0	2.0	0.0

completely converted the acids as there is almost no acid found in both fraction of catalytically produced bio-oil. This complete removal of the acids can significantly improve the handling properties of bio-oil. The aqueous fraction could be interesting for extraction and supercritical water gasification to produce hydrogen for hydrotreatment of the bio-oil [26,27].

3.2. Catalyst regeneration characteristics

After each experiment, the catalyst was regenerated by combustion of the coke deposited on the catalyst. After the first regeneration, the catalyst showed an activity similar to the fresh catalyst. After the second regeneration, the catalyst showed some loss of activity and partly irreversible deactivation of the catalyst happened. To study the deactivation behavior of the catalyst, experiments were performed with second time regenerated catalyst and results were compared with that of the fresh catalyst. Two experiments were performed at 475 °C and 500 °C catalyst bed temperature to study the catalyst deactivation behavior. Comparison of product distribution on dry basis is presented in Fig. 4a. Second time regenerated catalyst shows similar trends at both reaction temperatures of 475 °C and 500 °C. A deactivated catalyst produced less coke and less gas and resulting in slightly higher liquid yields of both organic and aqueous fractions of the liquid. There was no noticeable

difference obtained in gas composition using both fresh and deactivated catalyst at reaction temperatures of 475 °C and 500 °C.

A very significant difference was noticed in properties of the organic fraction of liquid (Fig. 4b). Deactivated catalyst shows a relatively poor de-oxygenation of bio-oil. The catalyst used at higher reaction temperature showed a higher loss in its activity after regeneration. This loss in activity or deactivation of catalyst can be attributed to batch mode of catalyst application. As catalyst is employed for treatment of bio-oil vapors without continuous regeneration, the catalyst pores are completely blocked and show irreversible deactivation. In a commercial application, catalyst will be employed with efficient and continuous regeneration system and irreversible deactivation of catalyst is not likely to happen but needs to be checked. If we take example of an FCC process, the small pore zeolites are successfully regenerated without loss of their catalytic activity. Alumina having even large pore size is likely to show even better performance in a FCC kind of process for treatment for of bio-oil vapors.

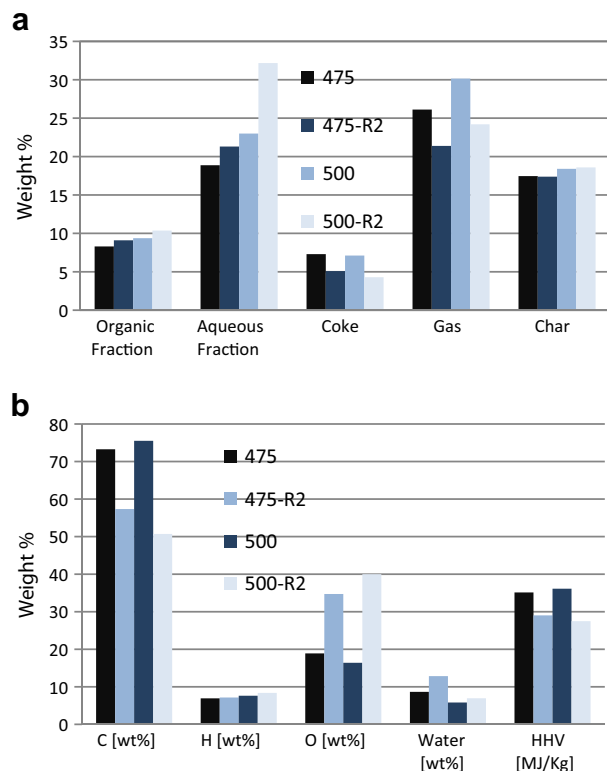


Fig. 4. a. Effect of catalyst deactivation on yields of different products. b. Effect of catalyst deactivation on the characteristics of organic fraction of the liquid. Experiments 475 and 500 are conducted with fresh catalyst and 475-R2 and 500-R2 are conducted with second time regenerated catalyst.

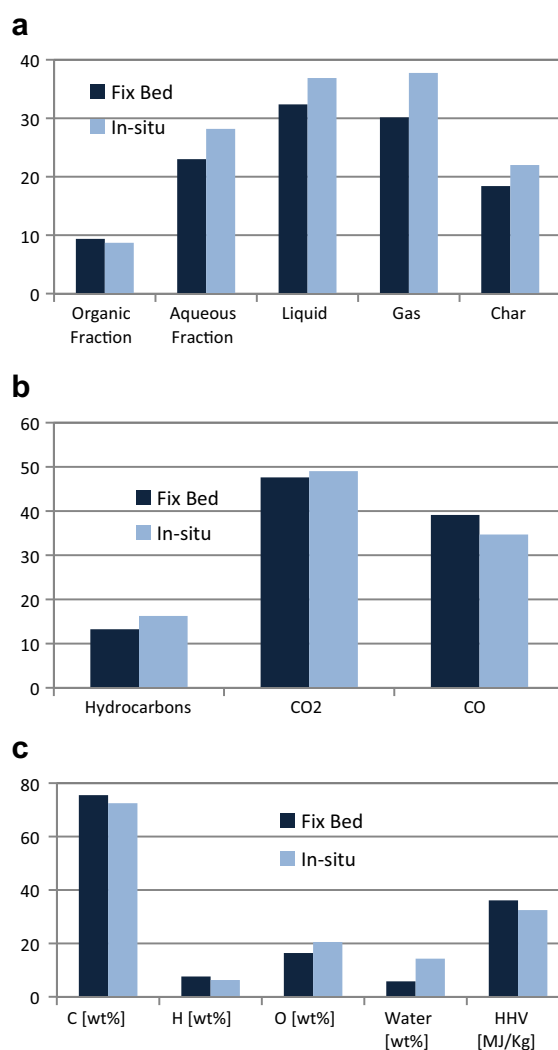


Fig. 5. a. Effect of catalytic pyrolysis mode on the yields of different products. b. Effect of catalytic pyrolysis mode on the gas composition. c. Effect of catalytic pyrolysis mode on the characteristics of organic fraction of the liquid.

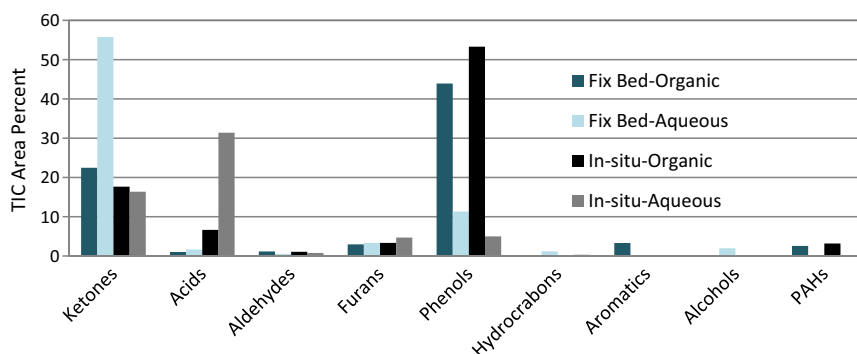


Fig. 6. Effect of catalytic pyrolysis mode on the chemical composition of the liquid.

3.3. In-situ catalytic upgrading of biomass pyrolysis vapors in an entrained flow reactor system

In the previous section, results are presented for application of catalysts in a fixed bed reactor at the downstream of the pyrolysis reactor. The fixed bed catalyst system which was used to isolate the catalyst/vapor contact problems may occur in the case of in-situ application of the catalyst in an entrained down flow reactor, and to study the effect of the catalyst temperature independent of the pyrolysis reaction temperature. A fixed bed reactor system is not a viable option for commercial applications and also will result in a problem with respect to continuous regeneration of the catalyst compared to more common systems e.g. a fluid catalytic cracker (FCC) or a fluidized bed reactor system. Fluidized bed type systems are a common approach for catalytic pyrolysis of biomass at commercial scale, where the catalyst can partly or fully replace the heating media generally sand. To study in-situ catalytic flash pyrolysis of biomass, $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ was employed in an entrained down flow pyrolysis reactor. A good contact between the catalyst and the biomass is required for in-situ application. The catalyst was grounded and physically mixed with biomass in 1:1 ratio to have the same catalyst/biomass ratio that was used in the fixed bed catalysis. This premixed feedstock of biomass and the catalyst was fed to the pyrolysis reactor. As the temperature had no significant effect on activity and function of $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$, the in-situ catalytic pyrolysis experiments were conducted at 500 °C to optimize the biomass conversion and secondary cracking.

For comparison of fixed bed (post treatment) and in-situ application of catalyst, product distribution, gas composition and liquid characterization are presented in Fig. 5a, b, and c respectively. In-situ experiments led to higher gas and char yields, higher liquid yields with higher aqueous fraction and slight lower organic fraction yields. A higher char yield for the in-situ experiments is attributed to the coke formation on the catalyst. A higher gas yield for the in-situ experiments can be attributed to a higher secondary cracking due to a longer contact of the catalyst and the vapors for in-situ mode where the vapor/solid residence time is 4 s being much longer than 0.5 s in the catalyst fixed bed in the post treatment mode. The lower organic liquid yields for in-situ experiments can also be attributed to this higher secondary cracking of the vapors. The bio-oil (organic liquid) characteristics show slightly less de-oxygenation for in-situ experiment, this can be attributed to the relative poor catalyst/vapor contact in the in-situ mode. A decrease in the carbon and hydrogen contents of the bio-oil can be noticed with resulting higher oxygen and lower energy contents of bio-oil. This loss in hydrogen and carbon in bio-oil is attributed to the higher yields of hydrocarbon gas. A comparison of the chemical composition of the bio-oil in the different modes is presented in Fig. 6. The in-situ experiments result in slightly higher acids and phenols yields, while the rest of the compounds were either reduced or not changed. Higher acids yield can also be attributed to the relative poor catalyst/vapor contact

in the in-situ mode. For in-situ applications of the catalyst, a high catalyst/biomass ratio can compensate the poor catalyst/vapor contact. In the present work, the catalyst/biomass ratio could not further be increased due to practical operation limitations of the entrained down flow reactor system. However, in a commercial system like a fluidized bed, higher catalyst/biomass ratios can be implemented to improve the catalyst/vapor contact and to achieve a higher level of de-oxygenation.

4. Conclusions

It is evident that $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ is a promising catalyst to improve the deleterious properties of the bio-oil. A high level of de-oxygenation was achieved using both experimental modes of operation, post treatment of pyrolysis vapor and in-situ upgrading of pyrolysis vapors. The catalytically produced bio-oil had a high calorific value and was rich in valuable chemical compounds. Acids in the bio-oil were completely removed resulting in a neutral pH bio-oil that can improve handling and stability characteristics of the bio-oil. Such a remarkable improvement in quality of bio-oil is of high significance towards production of a green fuel precursor. This high energy bio-oil, rich in organics, with low water and oxygen content can be upgraded via hydrotreatment for fuel application.

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